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SYNTHESIS AND CHARACTERIZATION OF NEW PHOSPHAZENE  
POLYMERS(U) TEXAS CHRISTIAN UNIV FORT WORTH DEPT OF  
CHEMISTRY R H NEILSON ET AL 21 JAN 88 ARO-24179 19-CH  
DAAG29-84-K-0147

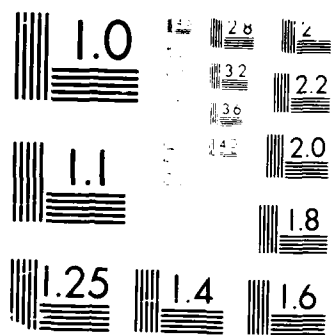
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## REPORT DOCUMENTATION PAGE

AD-A191 508

1b. RESTRICTIVE MARKINGS

3. DISTRIBUTION/AVAILABILITY OF REPORT

Approved for public release;  
distribution unlimited.

2b. DECLASSIFICATION/DOWNGRADING SCHEDULE

4. PERFORMING ORGANIZATION REPORT NUMBER(S)

Final Report, 1985-1987

5. MONITORING ORGANIZATION REPORT NUMBER(S)

ARU 24179.19-CH

6a. NAME OF PERFORMING ORGANIZATION  
Texas Christian University  
Department of Chemistry6b. OFFICE SYMBOL  
(If applicable)

7a. NAME OF MONITORING ORGANIZATION

U. S. Army Research Office

6c. ADDRESS (City, State, and ZIP Code)

Fort Worth, Texas 76129

7b. ADDRESS (City, State, and ZIP Code)

P. O. Box 12211  
Research Triangle Park, NC 27709-22118a. NAME OF FUNDING/SPONSORING  
ORGANIZATION  
U. S. Army Research Office8b. OFFICE SYMBOL  
(If applicable)

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

DAAG29-84-K-0147

8c. ADDRESS (City, State, and ZIP Code)

P. O. Box 12211  
Research Triangle Park, NC 27709-2211

10. SOURCE OF FUNDING NUMBERS

PROGRAM  
ELEMENT NO.PROJECT  
NO.TASK  
NO.WORK UNIT  
ACCESSION NO.

11. TITLE (Include Security Classification)

Synthesis and Characterization of New Phosphazene Polymers

12. PERSONAL AUTHOR(S)

R.H. Neilson and P. Wisian-Neilson

13a. TYPE OF REPORT

Final

13b. TIME COVERED

FROM 1984 TO 1987

14. DATE OF REPORT (Year, Month, Day)

1/21/1988

15. PAGE COUNT

21

16. SUPPLEMENTARY NOTATION

The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES

FIELD

GROUP

SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

Phosphazene

Phosphoranimine

Polymer

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report describes results obtained in detailed studies of the synthesis, characterization, and chemical reactivity of poly(alkyl/aryl)phosphazenes, a new class of phosphazene polymer. Lists of personnel supported on this contract and the publications arising from it are included.

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SELECTED  
FEB 23 1988  
S CH D

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT

☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION

Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL

22b. TELEPHONE (Include Area Code)

22c. OFFICE SYMBOL

# **Synthesis and Characterization of New Phosphazene Polymers**

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**January 20, 1988**

**Final Report**

**U. S. ARMY RESEARCH OFFICE**

**Contract No. DAAG29-84-K-0147**

**Department of Chemistry  
Texas Christian University  
Fort Worth, Texas 76129**

**and**

**Department of Chemistry  
Southern Methodist University  
Dallas, Texas 75275**

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# Synthesis and Characterization of New Phosphazene Polymers

## Introduction

In recent years, many poly(phosphazenes),  $[R_2PN]_n$ , with a variety of substituents at phosphorus have been prepared and they often exhibit useful properties including low temperature flexibility, resistance to chemical attack, flame retardancy, stability to UV radiation, and reasonably high thermal stability.<sup>1,2</sup> Compounds containing biologically, catalytically, or electrically active side groups are also being investigated.<sup>3,4</sup>

The most commonly used synthetic route to poly(phosphazenes) is the ring-opening/substitution method developed by Allcock and coworkers.<sup>1</sup> This procedure involves the initial preparation of poly(dichlorophosphazene),  $[Cl_2PN]_n$ , by the ring-opening polymerization of the cyclic trimer and subsequent nucleophilic displacement of the chlorine atoms along the chain. In each case, the substituents at phosphorus must be introduced after polymerization since the fully substituted cyclic phosphazenes do not polymerize.<sup>5,6</sup>

A common feature of poly(phosphazenes) prepared in this manner is that the organic substituents are bonded to phosphorus through oxygen or nitrogen links, thereby providing pathways for decomposition or depolymerization on heating above about 200°C. It has been postulated that directly P-C bonded alkyl or aryl side groups might enhance the thermal or chemical stability of the polymers and give rise to interesting physical properties.<sup>6,8</sup> Furthermore, the alkyl substituted poly(phosphazenes),  $[R_2PN]_n$ , are isoelectronic with the well-known siloxane polymers,  $[R_2SiO]_n$ , and the extent of this analogy would be interesting to pursue. The published attempts to prepare the directly P-C bonded polymers by the substitution method have generally not been successful. Treatment of poly(dihalophosphazenes) with organometallic reagents (e.g.,  $RMgX$  or  $RLi$ ) results in either incomplete substitution under mild conditions or undesired reactions such as chain cleavage and/or crosslinking under more vigorous conditions.<sup>7-10</sup>

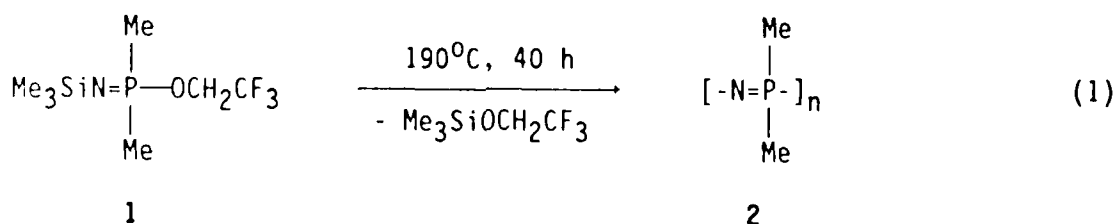
During the last few years, a new general method for the synthesis of poly(phosphazenes) has been under investigation in our laboratory. The approach is based on the premise that suitably constructed N-silylphosphoranimines can eliminate substituted silanes to form cyclic and/or linear phosphazenes (eq 1). This type of *condensation polymerization* reaction has several potential advantages, the most important of which is the ability to incorporate the desired phosphorus substituents directly into the starting Si-N-P compound. This procedure has resulted in the successful preparation of the first fully P-C bonded poly(phosphazene),  $[Me_2PN]_n$ , as described in preliminary reports.<sup>11-13</sup>

We report here the results of our recent studies of poly(alkyl/arylphosphazenes) with particular emphasis on the following areas: (1) the overall scope of, and improvements in, the condensation polymerization method; (2) the characterization of a representative series of these polymers by dilute solution techniques (viscosity, membrane osmometry, light scattering, and size exclusion chromatography), thermal analysis (TGA and DSC), NMR spectroscopy, and X-ray diffraction; (3) the preparation and preliminary thermolysis reactions of new, functionalized phosphoranimine monomers; (4) the mechanism of the polymerization reaction; and (5) the derivative chemistry of the preformed poly(alkyl/arylphosphazenes).

## Synthesis of Poly(alkyl/arylphosphazenes)

### A. Condensation Polymerization of N-Silylphosphoranimines

In 1980, we reported<sup>11</sup> that N-trimethylsilyl-P,P-dimethyl-P-trifluoroethoxyphosphoranimine **1** undergoes a smooth thermal decomposition (eq 1) to afford poly(dimethylphosphazene) **2** in essentially

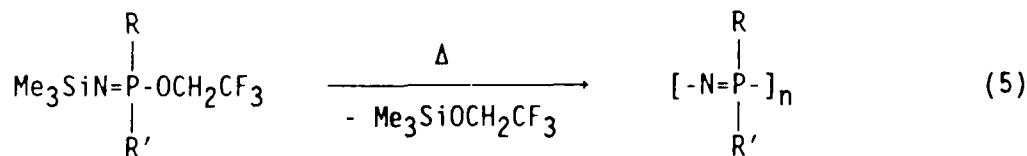
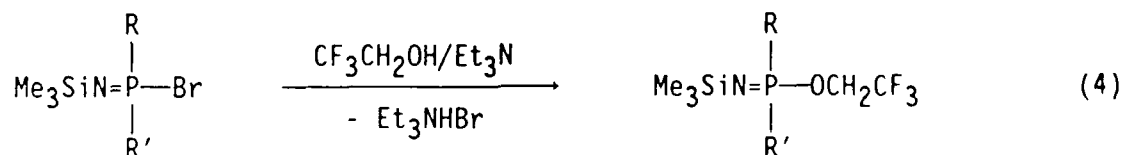
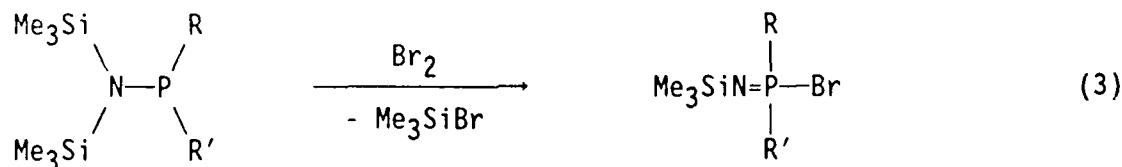
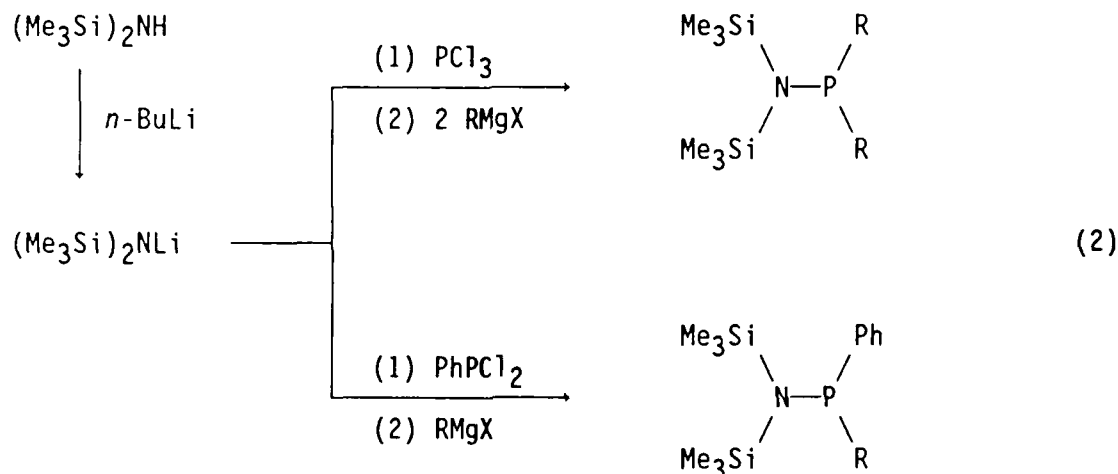


quantitative yield, free of the cyclic analogues. The product **2**, a white film-forming thermoplastic ( $T_g = -46^\circ\text{C}$ ,  $T_m = 143^\circ\text{C}$ ), bore a superficial resemblance to the material reported by Sisler<sup>14</sup> but it had a substantially higher molecular weight ( $M_w = 50,000$ ) and was better characterized by NMR spectroscopy and thermal analysis. Subsequent work in our laboratories, some of which has been reported,<sup>15-20</sup> has demonstrated that

the thermal decomposition of N-silyl-P-trifluoroethoxyphosphoranimines is indeed a general, high yield synthesis of poly(alkyl/arylphosphazenes). By designing the appropriate precursors, it is possible to widely vary the pattern of alkyl/aryl substituents along the polymer backbone, and, therefore, to essentially tailor the properties of the polyphosphazene products.

Most of the N-silyl-P-trifluoroethoxyphosphoranimine reagents, used as "monomers" in this polymer synthesis, are readily prepared from either  $\text{PCl}_3$  or  $\text{PhPCl}_2$  in a straightforward, 3-step reaction sequence (eqs 2-4).<sup>18,21,22</sup> These compounds are obtained as colorless, distillable, air-sensitive liquids in yields of 50-75% based on starting  $\text{PCl}_3$  or  $\text{PhPCl}_2$ . Some of the precursors (e.g.,  $\text{R} = \text{Me}$ ,  $\text{R}' = \text{Et}$ ,  $\text{CH}_2\text{CH}_2\text{Ph}$ ) are actually obtained by a side group modification of a simpler phosphoranimine such as 1. Further details of the preparative chemistry of these precursors and related compounds will be discussed in a later section of this report.

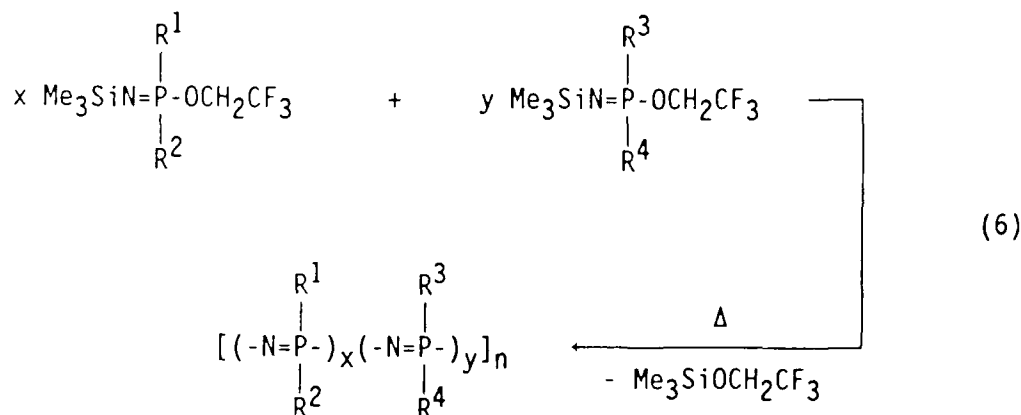
On heating at ca. 160-200°C for 2-12 days in sealed, evacuated glass or stainless steel vessels, these phosphoranimines quantitatively eliminate the silyl ether byproduct,  $\text{Me}_3\text{SiOCH}_2\text{CF}_3$ , to form the poly(alkyl/arylphosphazenes). The synthesis of a representative series of the homopolymers (i.e., products derived from a single precursor) is shown in equation 5. As will be discussed in more detail later, the properties of these polymers are found to be very dependent upon the nature of the substituents along the polymer backbone.



R	Me	Et	<sup>n</sup> Pr	Me	Me	Me	Me	Et	CH <sub>2</sub> Ph
R'	Me	Et	<sup>n</sup> Pr	Et	<sup>n</sup> Pr	CH <sub>2</sub> CH <sub>2</sub> Ph	Ph	Ph	Ph

In addition to the synthesis of a wide variety of homopolymers, the condensation polymerization of N-silyl-P-trifluoroethoxyphosphoranimines can also be used to prepare other types of poly(alkyl/aryl-phosphazenes) including: (1) copolymers of variable composition, (2) polymers containing certain functional groups such as pendent phosphine ligands, and (3) crosslinked polymers. Each of these variations will be briefly described below.

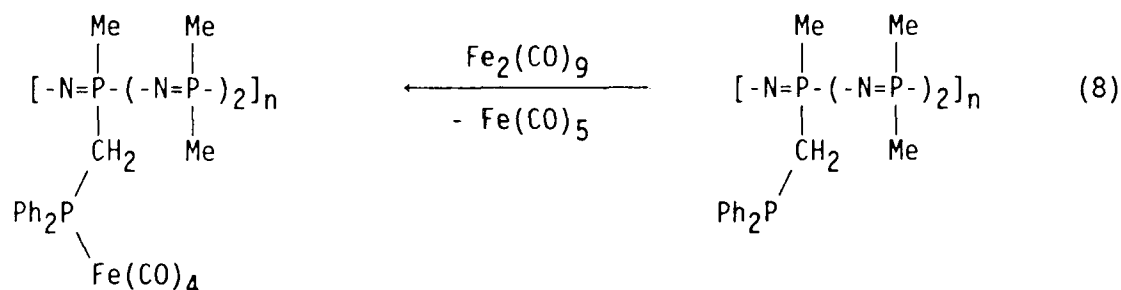
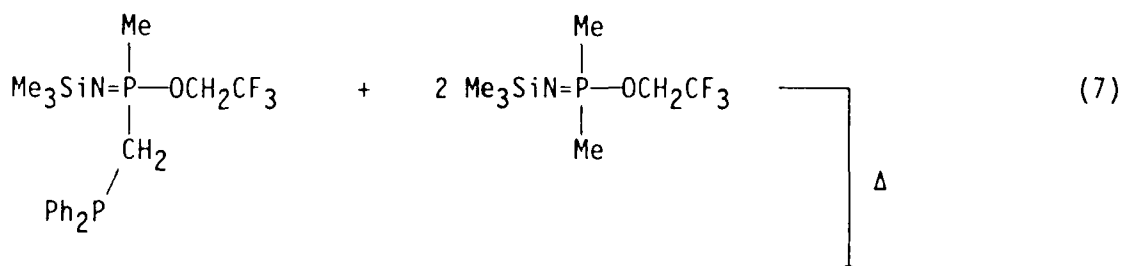
Copolymers are easily prepared by heating a mixture of two (or presumably more) N-silylphosphoranimines containing the desired combination of alkyl/aryl groups.<sup>12,15,16</sup> Since most of the precursors decompose at comparable rates, the polymer composition is easily controllable by adjusting the stoichiometry (x:y) of the starting mixture. Several of the types of copolymers prepared in this manner are summarized in equation 6. In most cases, the monomer ratio (x:y) has been varied from ca. 1:5 to 5:1, thereby yielding a large number of copolymers having a broad spectrum of properties (i.e., solubilities, glass transition temperatures, viscosities, thermal stabilities, etc.). Typically, the molecular weights ( $M_w$ ) of both the homo- and copolymers are in the range of ca. 50,000 - 250,000 and the molecular weight distributions are relatively narrow ( $M_w/M_n \approx 1.5 - 2.5$ ). The detailed characterization of a representative series of these poly(alkyl/arylphosphazenes) is discussed in the next section.



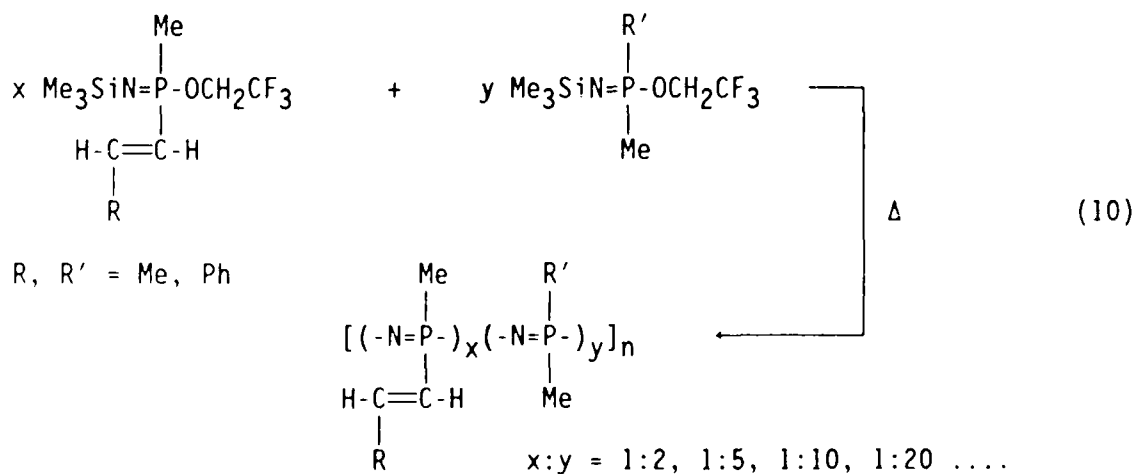
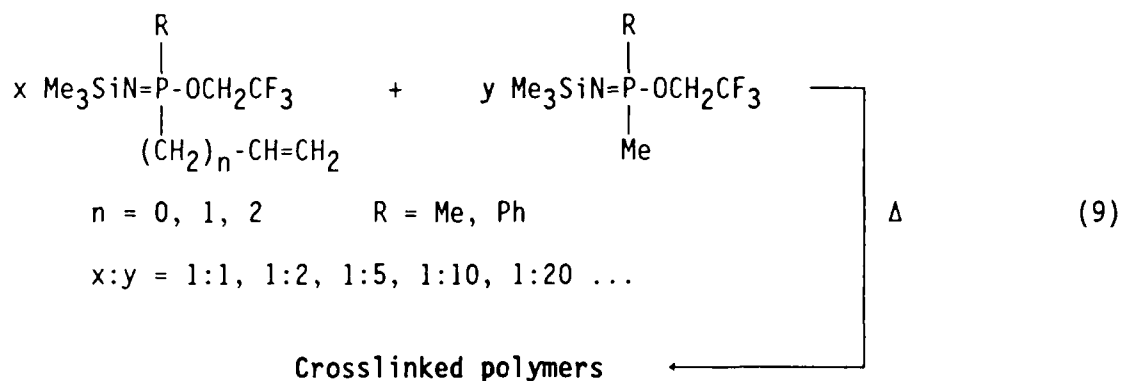
R <sup>1</sup>	Me	Me	Me	Me	Me	Me	Me	Me	Me	Et
R <sup>2</sup>	Me	Me	Me	Me	Me	Me	Ph	Ph	Ph	Et
R <sup>3</sup>	Me	Et	<sup>n</sup> Pr	Me	Me	Me	Me	Me	<sup>n</sup> Pr	Et
R <sup>4</sup>	Ph	Et	<sup>n</sup> Pr	Et	<sup>n</sup> Pr	CH <sub>2</sub> CH <sub>2</sub> Ph	CH <sub>2</sub> CH <sub>2</sub> Ph	<sup>n</sup> Pr	<sup>n</sup> Pr	Ph

Poly(alkyl/arylphosphazenes) that contain chemically reactive substituents can, in principle, be prepared by introducing the desired functional groups either prior to polymerization by chemical modification of the simple N-silylphosphoranimines, or after polymerization by suitable derivative chemistry of a preformed poly(alkyl/arylphosphazene). The preparation of a variety of functionalized monomers and polymers are discussed later in this report. In practice, we find that, although a wide variety of functional groups can be readily incorporated into the monomers, many of these functionalized monomers do not polymerize cleanly. A case in point is the general failure of the C-silylated precursors<sup>23,24</sup> to undergo condensation polymerization. For reasons that are not yet clear, these silylated precursors are much more thermally stable than the parent dimethylphosphoranimine **1** and, under forcing conditions (ca. 220°C, for up to 21 days), they decompose to unidentified, intractable black solids rather than linear polymers. On the other hand, as will be discussed later, silyl groups can be easily attached to the preformed polymer  $[(\text{Ph})(\text{Me})\text{PN}]_n$  to give interesting, fully characterized materials.

The problem with the polymerization of the silyl substituted monomers is probably not steric in nature, since other precursors with fairly bulky groups do polymerize. For example, N-silylphosphoranimines bearing the (diphenylphosphino)methyl group,  $\text{Ph}_2\text{PCH}_2$ , undergo facile copolymerization with **1** to afford novel poly(alkyl/arylphosphazenes) of moderate molecular weight (ca. 50,000) which contain pendent phosphine ligands (eqs 7, 8).<sup>25,26</sup> The ability of such polymers to coordinate to metal centers, without chain degradation or crosslinking, was shown by their reactions with  $\text{Fe}_2(\text{CO})_9$  which gave the fully  $\text{Fe}(\text{CO})_4$ -complexed derivatives (eq 8).



A third variation in the condensation polymerization of N-silylphosphoranimines involves the preparation of crosslinked polymers. We have recently prepared a series of vinyl,<sup>27</sup> allyl,<sup>25,26</sup> and butenyl<sup>24</sup> substituted phosphoranimines and have studied their cothermolysis reactions (eq 9) with both the dimethyl and the methylphenyl derivatives. In all cases which involve an *unsubstituted vinyl group*, attached either directly to phosphorus or through (CH<sub>2</sub>)<sub>n</sub> spacers, the *crosslinking occurs during the polymerization process itself*. The products from such reactions are generally insoluble, tough, rubbery materials that form highly swollen gels upon treatment with organic solvents.

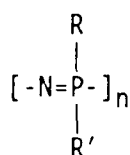


An alternative method,<sup>19</sup> which permits much better control over the degree of crosslinking in the poly(alkyl/arylphosphazenes), is based on the use of monomers containing 1,2-disubstituted olefinic groups (eq 10). In these cases, *soluble, uncrosslinked* copolymers are produced.

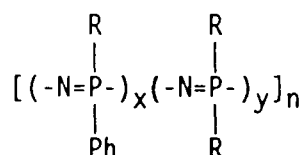
In summary, the condensation polymerization is a general, high yield synthesis of poly(alkyl/arylphosphazene) homopolymers, a wide variety of copolymers with easily controlled compositions, some types of functionalized polymers (e.g., with pendent phosphine ligands or substituted vinyl groups), and crosslinked, elastomeric materials.

### B. Characterization and Properties of Poly(alkyl/arylphosphazenes)

Recently, we have reported<sup>16</sup> the results of a reasonably complete study of the properties of a representative series of poly(alkyl/arylphosphazene) polymers (2-5) and copolymers (6 and 7), prepared by the condensation polymerization method. These new materials were characterized by high-field NMR spectroscopy, dilute solution techniques (viscosity, membrane osmometry, light scattering, and size exclusion chromatography), thermal analysis (DSC and TGA), and X-ray diffraction measurements. Some of the key findings, which present a fairly clear picture of the nature of these materials, are summarized in this section.



- 2: R = R' = Me  
3: R = R' = Et  
4: R = Me, R' = Ph  
5: R = Et, R' = Ph



- 6: R = Me  
7: R = Et  
x = y

**Solubility Properties.** As is the case with most poly(phosphazenes), the physical properties of these alkyl/aryl derivatives are found to be very dependent upon the nature of the substituents along the polymer backbone. This fact is illustrated, for example, by their solubility behavior. With the exception of poly(diethylphosphazene) (3),<sup>28</sup> which is insoluble in all common solvents, the new polymers are readily soluble in CH<sub>2</sub>Cl<sub>2</sub> and CHCl<sub>3</sub>, facilitating their characterization by NMR spectroscopy. In addition, the phenyl substituted compounds (4-7) are soluble in THF and various aromatic solvents. While none of the polymers are water-soluble, [Me<sub>2</sub>PN]<sub>n</sub> (2) is soluble in a 50:50 water/THF mixture.

**NMR spectral data.** All of the soluble polymers (e.g., 2 and 4-7) give high resolution NMR spectra that are completely consistent with their proposed structures.<sup>16</sup> The <sup>31</sup>P NMR spectra of the homopolymers 2, 4, and 5 consist of single peaks (with some fine structure noted for 4 and 5) as expected, while those of the copolymers 6 and 7 contain two distinct sets of resonances, corresponding to the two different structural environments of the phosphorus centers along the polymer backbone. As observed for other types of poly(phosphazenes)<sup>1-3</sup>, the <sup>31</sup>P chemical shifts of these alkyl/aryl substituted polymers are consistently ca. 15-30 ppm upfield from those of the analogous cyclic trimers and tetramers.

The <sup>1</sup>H NMR spectra of these polymers generally consist of relatively broad, featureless signals with the exception of the dimethyl compound 2 for which a sharp doublet is observed. In contrast, some important structural information is provided by <sup>13</sup>C NMR spectroscopy, particularly for the phenyl/alkyl derivatives 4 and 5. These materials are rare examples of poly(phosphazenes) that contain two different substituents at each phosphorus atom in the chain and, thus, have the possibility of being stereoregular. The fact that the structures are completely atactic, however, is clearly shown by the <sup>13</sup>C NMR spectral data. In particular, the high-field <sup>13</sup>C NMR spectrum of 4 contains three doublets in the P-Me region (ca. 22 ppm) in a 1:2:1 intensity ratio. This spectral feature clearly indicates a random stereochemistry of the side groups along the polymer backbone. The same reasoning accounts for the observation of three doublets (ca. 140 ppm) for the P-bonded phenyl carbon.

**Dilute solution characterization.** This series of poly(alkyl/arylphosphazenes) was also studied<sup>16</sup> by a variety of standard dilute solution techniques including viscosity measurements, membrane osmometry, size exclusion chromatography, and light scattering. Taken together, these studies demonstrate that the poly(alkyl/arylphosphazenes) exist as extended, flexible chains in good solvents such as THF or CHCl<sub>3</sub>, with average chain lengths of several hundred to a thousand repeat units and symmetrical molecular weight distributions ( $M_w/M_n \approx 2$ ).

For all of the soluble polymers, plots of reduced viscosity vs. concentration were quite linear at low concentration (ca. 0.1-1.0%) with Huggins constants in the range (ca. 0.30-0.45) characteristic of good polymer/solvent interactions. In order to investigate solvent effects in more detail, the viscosity of the phenyl/methyl polymer **4** was measured in a series of solvents (THF,  $\text{CHCl}_3$ , toluene, DMF, and THF containing 0.1% tetra-*n*-butylammonium bromide). The intrinsic viscosity ( $[\eta] \approx 0.41$  dL/g) and the Huggins constant remained essentially the same in  $\text{CHCl}_3$ , toluene, and THF (with or without the ammonium salt additive), thus showing all of these to be very good solvents for the polymer. In DMF, however,  $[\eta]$  decreased to 0.24 dL/g and the Huggins constant increased to 0.71, consistent with the polymer having a more tightly coiled structure in this polar solvent.

The absolute number average molecular weights ( $M_n$ ) of the same series of polymers were determined by membrane osmometry.<sup>16</sup> The molecular weights ( $M_n$ ) fall in the general range of 20,000-100,000, with those of the dimethyl (**2**) and phenyl/methyl (**4**) polymers and the corresponding copolymer (**6**) typically being greater than 50,000. The analogous phenyl/ethyl compounds (**5** and **6**) have somewhat lower molecular weights but, since they have not been studied as extensively, it is not known whether this is due to the greater steric bulk of the ethyl group or to other factors such as reaction time and/or temperature.

Until recently, the rapid and routine characterization of these poly(phosphazenes) was hindered by their anomalous behavior in size exclusion chromatography (SEC) experiments. The analysis of these materials was attempted on commercial columns, with either  $\mu$ Styragel or glass bead packings, at a variety of temperatures and concentrations. In addition, several different solvents including mixed solvent systems were investigated. In almost all cases, grossly distorted, severely tailing, non-reproducible chromatograms were obtained, suggestive of an adsorption type of interaction between the polymer and the column materials. We have found, however, that these SEC problems are completely circumvented by the addition of a small amount (ca. 0.1 weight percent) of an ionic species such as  $(n\text{-Bu})_4\text{NBr}$  to the THF mobile phase. Under these conditions, classic SEC behavior is observed and consistent, non-tailing chromatograms are obtained. Moreover, the molecular weights measured by SEC, relative to narrow molecular weight polystyrene standards, agree very well (within ca. 20-30%) with the values determined by membrane osmometry. Similar effects were observed with other ammonium salt additives in THF as well as in  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$  solution. The fact that the solution viscosity, as mentioned above, is unaffected by the presence of the salt shows that there has been no significant change in the nature of the polymer/solvent interaction. The exact reason for this dramatic improvement in the chromatography is not known, but we speculated<sup>16</sup> that the ionic solute simply prevents whatever type of polar interaction was occurring in the prior experiments. Other new findings (see Section IVC), relevant to this question, indicate that the backbone nitrogen sites in these poly(alkyl/arylphosphazenes) are more easily protonated than those in the more conventional polymers bearing alkoxy, aryloxy, or amino substituents.

The absolute weight average molecular weights ( $M_w$ ) of several samples of  $[\text{Ph}(\text{Me})\text{PN}]_n$  (**4**) from different preparations were determined by light scattering measurements in dilute THF solutions. The  $M_w$  values, which ranged from 73,000 to 202,000, were consistently (ca. 30%) higher than those obtained by SEC determinations. These results, when combined with the membrane osmometry data, confirmed that the SEC experiments provide valid representations of the molecular weight distributions of these poly(alkyl/arylphosphazenes). The second virial coefficients  $A_2$  determined by light scattering are quite consistent with the osmometry values. The radius of gyration  $\langle S^2 \rangle^{1/2}$  of the highest molecular weight sample was found to be 249 Å and the calculated ratio  $\langle S^2 \rangle^{1/2} / M_w^{1/2}$  (ca.  $0.31 \text{ Å}^2 \cdot \text{mol/g}$ ) is essentially identical to the value obtained for high molecular weight poly(dichlorophosphazene). Also, a good correlation between  $M_w$  (light scattering) and intrinsic viscosity was observed for  $[\text{Ph}(\text{Me})\text{PN}]_n$  (**4**) over the molecular weight range noted above. Thus, the Mark-Houwink relationship,  $[\eta] = K(M_w)^a$ , gave values of  $K = 1.44 \times 10^{-4}$  (with  $[\eta]$  in dL/g) and  $a = 0.66$ . These data again indicate a well solvated, extended-chain structure of the polymer in THF.

**Thermal analysis results.** Not surprisingly, thermal analysis experiments (DSC and TGA)<sup>16</sup> demonstrated that the nature of the substituents along the polymer backbone has a pronounced effects on properties such as glass transition and melting temperatures and on the overall thermal stability of these poly(alkyl/arylphosphazenes). The symmetrically substituted poly(dialkylphosphazenes) **2** and **3** showed sharp endothermic melt transitions, indicating a fairly high degree of crystallinity in the materials. On the other hand, none of the phenyl substituted polymers (**4** and **5**) or copolymers (**6** and **7**) showed a melt transition; therefore, the side group asymmetry disrupts the crystalline order in the solid state. The general amorphous nature of the phenyl/alkyl homopolymers **4** and **5** is consistent with their structures being assigned as atactic on the basis of  $^{13}\text{C}$  NMR spectroscopy (see above).

In DSC experiments, poly(dimethylphosphazene) (**2**) showed a glass transition of  $-46^\circ\text{C}$  which increased to  $-3^\circ\text{C}$  and  $37^\circ\text{C}$  for the 25% (**6**) and 50% (**4**) phenyl substituted analogues. A similar trend was noted for the phenyl/ethyl derivatives **5** and **7**, although poly(diethylphosphazene) itself did not exhibit a discernible

glass transition. Studies of a much larger series of polymers and copolymers (eqs 5 and 6) are currently underway in order to better understand the structure/property relationships common to the poly(alkyl/arylphosphazenes).

Thermogravimetric analysis (TGA) of these poly(phosphazenes) showed their decomposition onset temperatures in an inert atmosphere to be ca. 350 to 400°C, depending on the side group. These temperatures are ca. 25-75°C higher than that reported for commercial materials based on the fluoroalkoxy substituted polymer,  $[(CF_3CH_2O)_2PN]_n$ . Preliminary indications, therefore, are that the incorporation of directly P-C bonded alkyl and/or aryl groups does enhance the thermal stability of poly(phosphazenes), as anticipated. Interestingly, methyl rather than phenyl side groups yield the more stable materials, as shown by the results for polymers **2**, **4**, and **6** which were found to have the highest decomposition temperatures. We have also recently reported<sup>29</sup> that silylmethyl groups (i.e.,  $Me_3SiCH_2$ ) have a significant stabilizing influence.

**X-ray diffraction studies.** In our work, samples of the poly(dialkylphosphazenes) **2** and **3** displayed X-ray powder diffraction patterns characteristic of crystalline regions in the materials. The peaks in the diffraction of **2** were of lower amplitude and greater angular breadth than those of **3**, indicating that poly(diethylphosphazene) (**3**) is highly crystalline while poly(dimethylphosphazene) (**2**) is more amorphous with smaller crystalline zones. This high degree of crystallinity is probably responsible for the insolubility of **3** as noted above. All of the phenyl substituted polymers **4-7** were found to be amorphous in the X-ray diffraction studies, a result that is further evidence for an atactic structure of the poly(alkyl-phenylphosphazenes) **4** and **5** and for a random substitution pattern in the copolymers **6** and **7**.

### C. Polymerization Mechanism

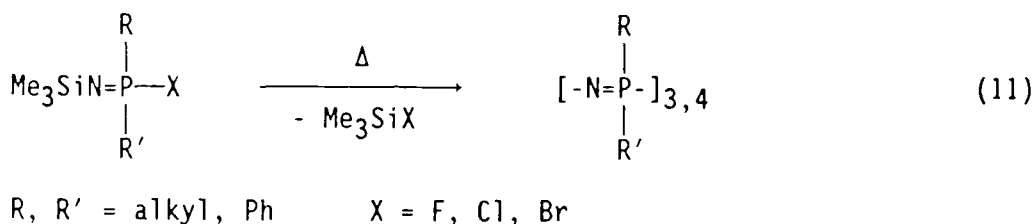
The successful synthesis of poly(alkyl/arylphosphazenes) by the condensation polymerization process leads to a number of questions concerning the mechanism of this reaction. For example, are cyclic or monomeric phosphazenes involved in the mechanism, or does the polymerization occur via a step growth or a chain growth process, and if so, what are the actual initiation, propagation, and termination steps? Although no detailed studies specifically aimed at elucidating the mechanism have been conducted, there are a number of experimental observations that are noteworthy in this context.

The possibility of cyclic trimers or tetramers being formed as intermediates can probably be eliminated from consideration. Allcock<sup>6</sup> has already shown that the permethylated cyclics do not thermally polymerize under a wide variety of conditions. Moreover, we have found that thermolysis of the dimethyl precursor **1** in the presence of the corresponding cyclics  $[Me_2PN]_{3,4}$  affords a mixture of unreacted cyclics and the dimethyl polymer **2** (presumably formed by the polymerization of **1**), indicating that condensation polymerization and ring-ring equilibration<sup>6</sup>/ring-opening occur by different mechanisms. It is more difficult to conclusively rule out the possibility of a monomeric phosphazene (e.g.,  $Me_2P\equiv N$ ) intermediate, especially since there is evidence for the existence of such a species, although it is stabilized by two bulky  $[(CH_3)_2CH]_2N$  substituents on phosphorus.<sup>30</sup> The formation of an unstable, monomeric  $R_2P\equiv N$  species in this polymerization process, however, is very unlikely. The major problem with this possibility is that it does not account for the preferential formation of polymers rather than the thermodynamically more stable cyclic trimers and tetramers. In fact, other transient, multiply-bonded species (e.g., the isoelectronic silanones,  $R_2Si=O$ ) invariably form cyclic oligomers rather than linear polymers when they are generated in the absence of trapping agents. A monomeric intermediate also seems to be inconsistent with the leaving group effects that are described below.

In organic polymer chemistry, most condensation polymerizations occur via a step growth mechanism in which the reactive functional groups condense with each other at a rate that is independent of molecular size. As a consequence, the reaction mixture consists of mainly short chain oligomers until very high degrees of conversion are achieved (e.g., when ca. 99% of the functional groups have reacted, the average polymer chain is only about 10 monomer units long). On the other hand, in a chain growth mechanism, the important reaction is that between the functional end of a growing polymer chain and a monomer molecule. This leads to the formation of high molecular weight polymer at the early stages of the reaction sequence.

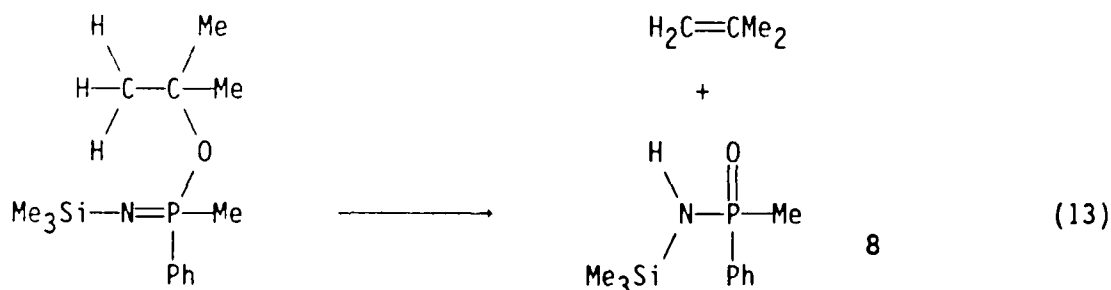
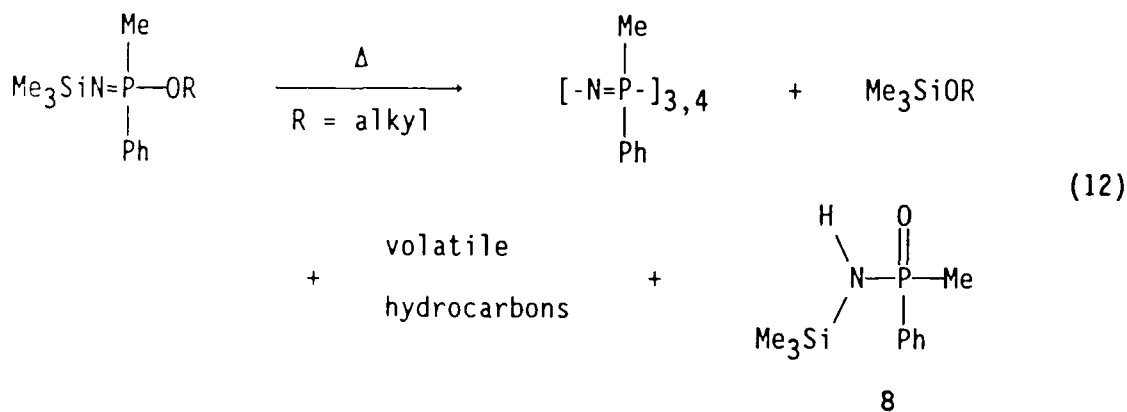
Initially, in our work, it was assumed that a typical step growth mechanism was operative for the polymerization of N-silylphosphoranimines since the polydispersity ( $M_w/M_n$ ) values of the poly(alkyl/arylphosphazenes) are close to the theoretical limit of 2.0, as expected for a step growth process. The possibility of a step growth mechanism is precluded, however, by results of experiments in which the polymerization was stopped prior to completion.<sup>16</sup> Even when the reaction is only ca. 20-50% complete, the reaction mixture consists of high molecular weight polymer ( $M_w \approx 60,000$ ) and unreacted monomer. No indication of the presence of smaller oligomers is found in the NMR and SEC studies of these reaction mixtures. These data clearly indicate that some type of a *chain growth mechanism must be occurring*.

Information is also available on how the nature of the leaving group (X) at phosphorus effects the thermal stability and/or decomposition products of the N-silylphosphoranimines,  $\text{Me}_3\text{SiN}=\text{P}(\text{X})\text{R}_2$ . The tendency of these precursors to thermally eliminate  $\text{Me}_3\text{SiX}$  follows the approximate order:  $\text{X} = \text{halogen} > \text{aryloxy} \approx \text{fluoroalkoxy} > \text{alkoxy} \approx \text{amino}$ . Thus, greater polarity of the  $\text{P}^{\delta+}-\text{X}^{\delta-}$  bond and the corresponding leaving group ability of  $\text{X}^-$  generally favor the elimination of  $\text{Me}_3\text{SiX}$ . As a result, the P-*halo*phosphoranimines often decompose during distillation when heated at relatively low temperatures (ca.  $150^\circ\text{C}$  or less) while most of the other types of phosphoranimines can routinely be distilled without decomposition.<sup>22,31</sup> The leaving group also has a pronounced influence on the type of phosphazene -- cyclic or polymeric -- that is formed in these condensation processes. For example, the N-silyl-P-*halo*phosphoranimines decompose to yield *cyclic* phosphazenes (eq 11), normally mixtures of trimers and tetramers, rather than polymers as obtained in the thermolyses of the trifluoroethoxy analogues (eqs 5, 6).

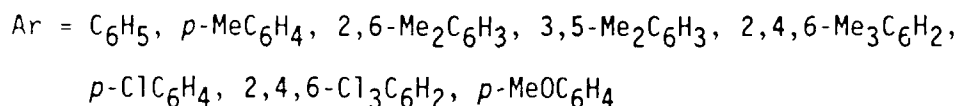
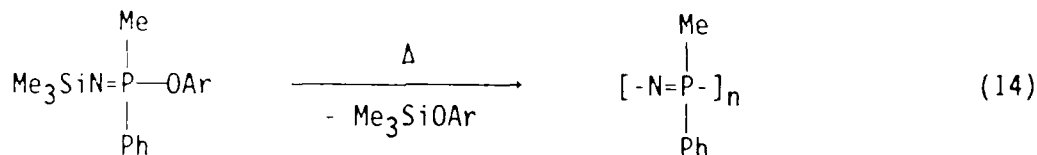


At first glance, such a dramatic leaving group effect might be interpreted as an indication that two different mechanisms were involved. Other unpublished work, however, showed that  $\text{Me}_3\text{SiBr}$  reacts with  $[\text{Me}_2\text{PN}]_n$ , prepared from the  $\text{P}-\text{OCH}_2\text{CF}_3$  derivative, at high temperature (ca.  $180^\circ\text{C}$ ) to cause chain degradation and formation of cyclic phosphazenes. This observation illustrates the principle that condensation reactions must produce an "inert" byproduct in order to be useful for polymerization reactions. Apparently, trifluoroethoxy- but not halosilanes are suitable elimination products in this sense.

These mechanistic questions, as well as the relatively high price of trifluoroethanol, led to an investigation of other alkoxy and aryloxy substituents as possible leaving groups.<sup>18,19,32</sup> Some unexpected as well as some useful results were obtained. When non-fluorinated *alkoxy* groups are attached to phosphorus, the precursors are much more thermally stable than the  $\text{OCH}_2\text{CF}_3$  derivatives. Furthermore, when more drastic conditions are used, the P-*alkoxy* compounds decompose to yield *cyclic* phosphazenes along with other products (eq 12). For example, in the thermolysis of the *t*-butoxy derivative (eq 13), the formation of the silylamino)phosphine oxide **8** probably occurs via a  $\beta$ -elimination of *isobutylene*.



We have also prepared a large series of P-aryloxyphosphoranimines by treatment of the P-bromophosphoranimine,  $\text{Me}_3\text{SiN}=\text{P}(\text{Me})(\text{Ph})\text{Br}$ , with the appropriate phenol derivative in the presence of  $\text{Et}_3\text{N}$ .<sup>19,32</sup> In contrast to the results obtained with the alkoxy analogues, **the thermal decomposition of the aryloxy substituted monomers is an efficient, high yield, and inexpensive new preparative route to the poly(alkyl/arylphosphazenes)** (eq 14). The difference between these systems (i.e., alkoxy vs aryloxy leaving groups) can be attributed to the inability of the aryloxy (or  $\text{OCH}_2\text{CF}_3$ ) groups to undergo  $\beta$ -elimination and to the fact that  $\text{ArO}^-$  is a better leaving group than  $\text{RO}^-$ .

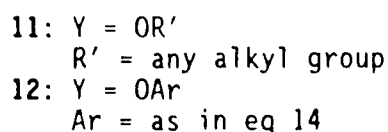
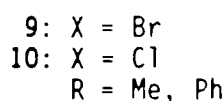
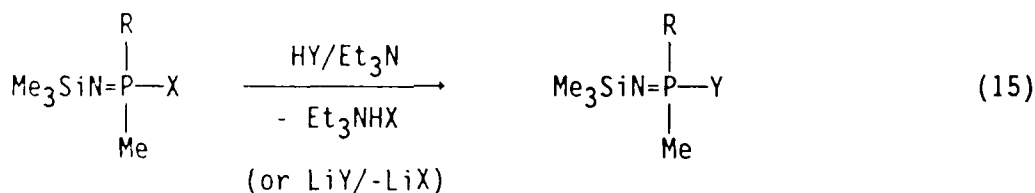


In a general sense, therefore, the formation of poly(alkyl/arylphosphazenes) by the thermolysis of N-silylphosphoranimines appears to occur via a chain growth process involving bimolecular reactions of the polar  $\text{P}^{\delta+}-\text{X}^{\delta-}$  and  $\text{N}^{\delta-}-\text{Si}^{\delta+}$  functional groups. Studies of the effects of variation of the leaving group (X) suggest that initiation may involve heterolytic cleavage of the P-X bond (i.e., formation of  $\text{X}^-$ ). Further conclusions about the exact nature of the propagation and termination steps (and, eventually, a means of controlling the degree of polymerization) will require more detailed mechanistic studies.

#### D. Functionalized N-Silylphosphoranimines

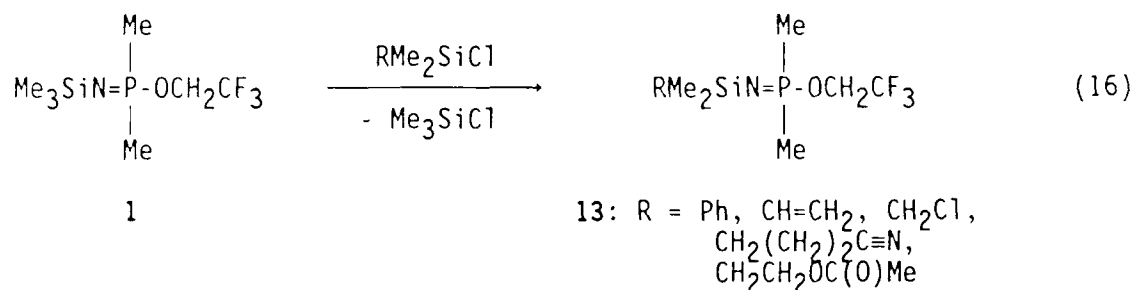
Virtually all of the products of the oxidation reactions of the (silylamino)phosphines described in the preceding section are N-silylphosphoranimines of general formula  $\text{Me}_3\text{SiN}=\text{P}(\text{X})\text{RR}'$ . As we have discussed earlier (Section III), some of these types of compounds are very useful precursors to both cyclic (X = halogen or alkoxy) and polymeric (X = fluoroalkoxy or aryloxy) phosphazenes. Because of their importance as precursors to poly(alkyl/arylphosphazenes), we have undertaken an extensive survey of the derivative chemistry of these N-silylphosphoranimines. The major objectives of this work are (1) to study the effects of leaving group (X) variation in order to improve and optimize the polymerization process and to further elucidate the polymerization mechanism; and (2) to introduce functional groups into the polymer precursors. In principle, there are three sites for variation of the structure of the N-silylphosphoranimine: the leaving group (X), the silyl group attached to nitrogen, and the other substituents (R, R') attached to phosphorus. All of these cases have been studied in some detail and examples of each are described below.

First, a wide range of potential leaving groups [e.g., Y = OR (11), OAr (12)]<sup>22,32</sup> can be easily introduced by straightforward nucleophilic substitution reactions of the readily available P-bromo- (9) or P-chloro- (10) phosphoranimines. Dialkylamino<sup>22</sup> and  $\text{PhS}$ <sup>32</sup> groups can also be incorporated into the compounds by similar substitution reactions, although these phosphoranimines are too thermally stable to be useful as phosphazene precursors.

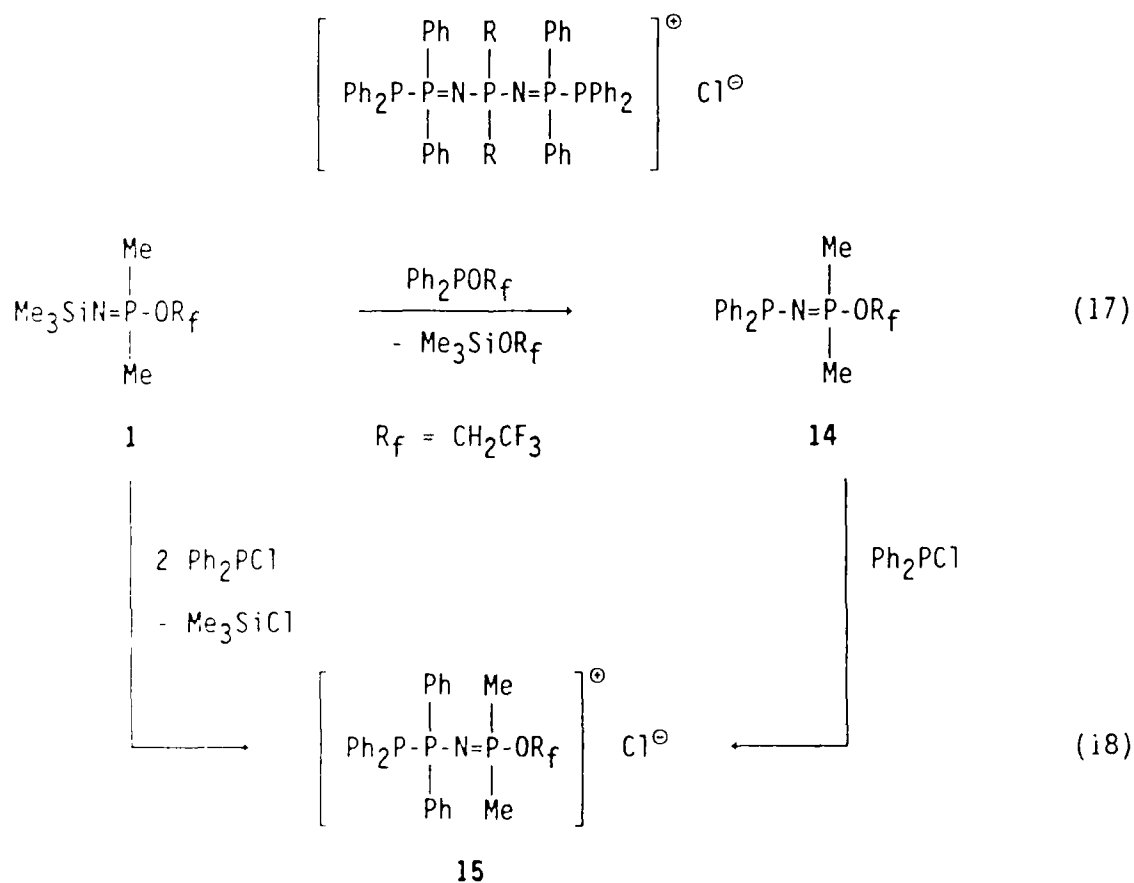


Second, the Si-N bond in these N-silylphosphoranimines is subject to cleavage by a variety of

reagents via nucleophilic attack at silicon. A particularly straightforward example of this mode of reactivity is the process of transsilylation (eq 16)<sup>33</sup> in which the phosphazene precursor **1** is smoothly converted into a series of Si-functionalized derivatives **13**. These reactions proceed rapidly at 0°C in CH<sub>2</sub>Cl<sub>2</sub> solution to give high yields (ca. 65-85%) of the transsilylated products. In similar fashion, compound **1** reacts in a 2:1 stoichiometry with dichlorosilanes to give the bis(phosphoranimino)silanes, [Me<sub>2</sub>(CF<sub>3</sub>CH<sub>2</sub>O)P=N]<sub>2</sub>E, where E = -Me<sub>2</sub>Si-, -SiMe<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>2</sub>-, and -SiMe<sub>2</sub>(OSiMe<sub>2</sub>)<sub>n</sub>SiMe<sub>2</sub>- (n = 0, 1, 2, 3, 4).<sup>33</sup>



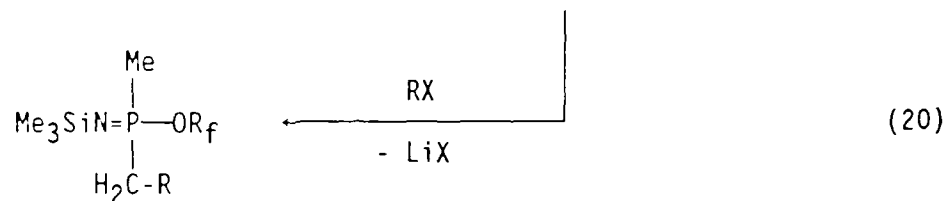
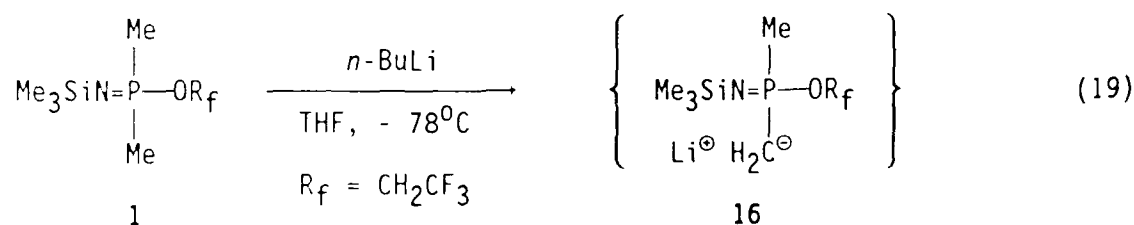
The Si-N bond in phosphoranimines such as **1** is also susceptible to cleavage by other polar reagents. Diphenyl(trifluoroethoxy)phosphine, for example, reacts cleanly with **1** to yield the P<sup>III</sup>-N=P<sup>V</sup> derivative **14** (eq 17) which, in turn will add a molecule of chlorodiphenylphosphine (eq 18) to yield the phosphonium salt **15**.<sup>34,34</sup> Alternatively, **15** can be produced in a single step by the reaction of **1** with two equivalents of Ph<sub>2</sub>PCl. This type of Si-N bond cleavage/quaternarization reaction had been reported earlier for simpler N-silylphosphoranimines, Me<sub>3</sub>SiN=PR<sub>3</sub>, without a functional group on phosphorus.<sup>35</sup> In related work,<sup>34</sup> we have found that more highly silylated phosphoranimines, e.g., (Me<sub>3</sub>Si)<sub>2</sub>N-PR<sub>2</sub>=NSiMe<sub>3</sub>, undergo similar reactions with chlorophosphines to give novel multiphosphorus ionic species of the following type.



The third type of derivatization reaction of the N-silylphosphoranimines is the one most relevant to the synthesis of poly(alkyl/arylphosphazenes). This involves chemical modification of the phosphorus-bonded alkyl side groups in the actual condensation monomers such as Me<sub>3</sub>SiN=P(OCH<sub>2</sub>CF<sub>3</sub>)Me<sub>2</sub> (**1**). There are two

primary reasons for doing this type of derivative chemistry: (1) to obtain polymer precursors having a greater variety of functional groups, and (2) to develop useful model reactions for similar chemistry to be later applied to the preformed poly(alkyl/arylphosphazenes) as discussed in Section IV.

It was reported by Schmidbaur<sup>36</sup> that the permethylated N-silylphosphoranimine,  $\text{Me}_3\text{SiN}=\text{PMe}_3$ , could be converted to the silyl derivative,  $\text{Me}_3\text{SiN}=\text{P}(\text{CH}_2\text{SiMe}_3)\text{Me}_2$ , by treatment with *n*-BuLi followed by  $\text{Me}_3\text{SiCl}$ . As described earlier (Section IVA), similar deprotonation/substitution reactions can be carried out on methyl substituted cyclic and polymeric phosphazenes. Allcock<sup>37</sup> has reported, however, that phosphazenes bearing *trifluoroethoxy* groups undergo facile dehydrofluorination upon reaction with *n*-BuLi and various electrophiles. Recent work in our laboratories<sup>23-26</sup> has shown that, if mild conditions are employed, the methyl group in the phosphazene precursors such as  $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)\text{Me}_2$  (**1**) can be selectively deprotonated by *n*-BuLi (eq 19) to yield the carbanion intermediate **16**. Solutions of the anion **16** in THF, which are stable up to ca. -50°C, have been treated with a variety of alkyl,<sup>38</sup> phosphinyl,<sup>25</sup> and silyl<sup>23</sup> halides to afford high yields of the functionalized phosphoranimines **17**, **18**, and **19**, respectively (eq 20). Quenching of the anion **16** with bromine produces the bromomethyl derivative **18** (eq 20).



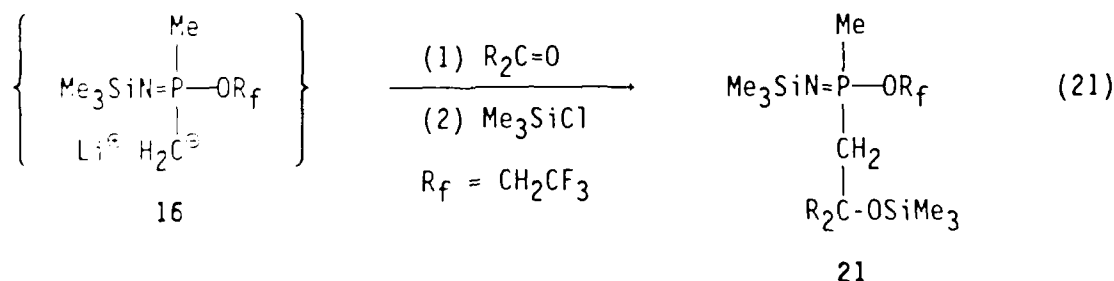
17: R = Me,  $\text{CH}_2\text{Ph}$ ,  $\text{CH}_2\text{CH}=\text{CH}_2$

18: R =  $\text{PPh}_2$ ,  $\text{P}(\text{NMe}_2)_2$

19: R =  $\text{SiMe}_2\text{R}'$  [ $\text{R}' = \text{Me}$  (a),  $\text{Ph}$  (b),  $\text{H}$  (c),  $\text{CH}=\text{CH}_2$  (d),  $\text{CH}_2(\text{CH}_2)_2\text{C}\equiv\text{N}$  (e)]

20: R = Br

The carbanion **16** also reacts smoothly with other common organic electrophiles including aldehydes and ketones (eq 21).<sup>38</sup> In this series of reactions, the intermediate alkoxy anion was quenched with  $\text{Me}_3\text{SiCl}$  to give the C-siloxy derivatives **21**. This type of reaction is a good model system for the preparation of the alcohol substituted poly(alkyl/arylphosphazenes).

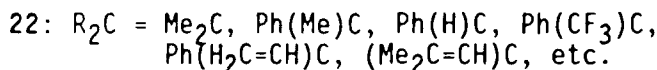
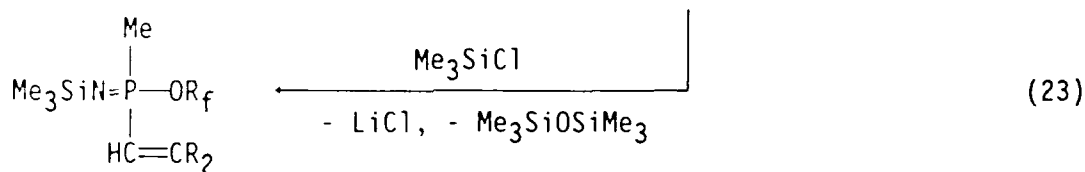
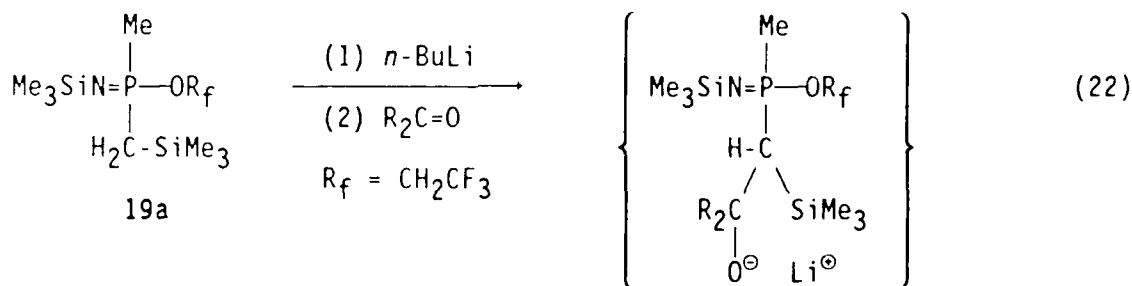


$\text{R}_2\text{C}(\text{O}) = \text{MeC}(\text{O})\text{Me}$ ,  $\text{PhC}(\text{O})\text{Me}$ ,  $\text{PhC}(\text{O})\text{H}$ ,  $\text{MeC}(\text{O})\text{CH}=\text{CH}_2$

The thermal decomposition reactions of most of these functionalized N-silylphosphoranimines have been studied. In many cases (e.g., the silylated compounds **19**), they are found to be more thermally stable than their simple precursors (e.g., **1**) and, thus, do not polymerize.<sup>23</sup> On the other hand, the diphenylphos-

phine derivative **18** does copolymerize with the dimethyl monomer **1** as described earlier (eqs 7, 8) to yield poly(alkyl/arylphosphazenes) bearing pendent phosphine ligands. Metal carbonyl complexes of both the polymer bound phosphines (eq 8) and the precursor model compounds **18** have been prepared.<sup>25,26,32</sup>

In spite of the fact that they do not undergo the condensation polymerization reaction, the C-silylated phosphoranimines **19** are synthetically useful compounds. For example, they can be used in the Peterson olefination reaction in which the carbon  $\alpha$  to silicon is easily deprotonated and then treated with carbonyl compounds (eq 22). The 1,2-elimination of  $\text{LiOSiMe}_3$  (which is then quenched with  $\text{Me}_3\text{SiCl}$ ) leads to high yields of the vinyl substituted N-silylphosphoranimines **22** (eq 23).<sup>19,34</sup>



Thus, by a combination of two successive deprotonation/substitution reactions (eqs 19-20 and 22-23), the easily prepared dimethylphosphoranimine **1** can be converted to a wide variety of new precursors to poly(alkyl/arylphosphazenes) which contain vinyl groups having virtually any substituent pattern that is desired. The condensation polymerization reactions of a few of these precursors **22** have been carried out, leading to several copolymers containing pendent vinyl groups (eq 10).<sup>19,34</sup>

The chemistry of these N-silylphosphoranimines is, indeed, very diverse and has led to the synthesis of many different types of derivatives bearing functional groups at carbon, nitrogen, and silicon. Some of these compounds such as the phosphine derivatives **18** and the vinyl systems **22** are themselves very useful as condensation monomers for the synthesis of new functionalized poly(alkyl/arylphosphazenes), while others (e.g., the C-silyl derivatives **19**) are important as precursors to new monomers (e.g., **22**). Also, reactions involving cleavage of the Si-N bond in these systems can lead to a many new element-nitrogen-phosphorus compounds such as transsilylation products and  $\text{P}_x\text{N}_y$  cations. A variety of other types of reactions of these multifaceted reagents are currently under investigation.

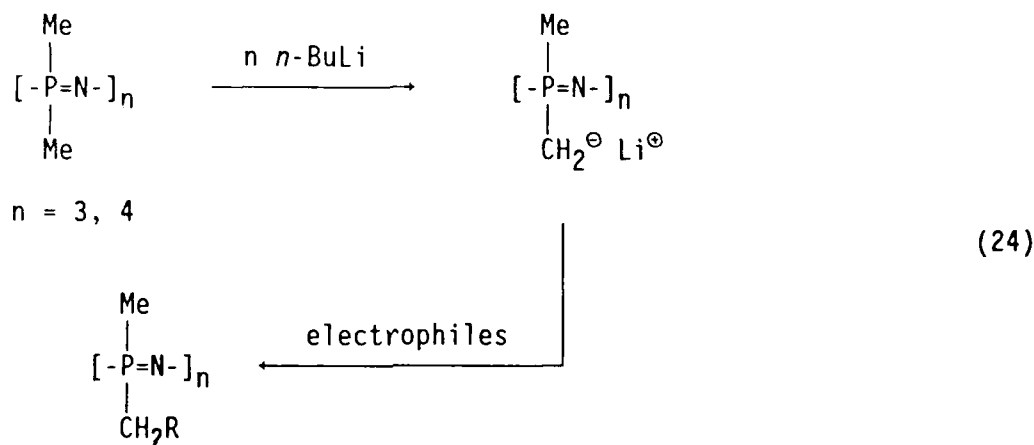
## Chemistry of Poly(alkyl/arylphosphazenes)

With the ready availability of a large number of poly(alkyl/arylphosphazenes), it is of interest to study the chemistry of these polymers in order to compare their reactivity to the amino, alkoxy, and aryloxy substituted polymers and to diversify the types of substituents that can be attached directly to the backbone by P-C linkages. The latter reason is particularly important because the thermal, solubility, mechanical, surface, and chemical properties can be drastically altered by changing the nature of the side groups on the backbone. Furthermore, the attachment of various functional groups to the polymers offers potential sites for crosslinking, binding of transition metal catalysts, and interaction with biological systems. Indeed, it is the numerous examples of the variety of properties of, and the incorporation of reactive functional groups into, the derivatives of  $[\text{Cl}_2\text{PN}]_n$  that account for the uniqueness of polyphosphazenes among polymer systems. The results to be discussed in this section indicate that the more recently discovered poly(alkyl/arylphosphazenes) are likely to have a derivative chemistry which is similar in diversity and utility to that of poly(dichlorophosphazene).

There are three potentially reactive sites in the simple poly(alkyl/arylphosphazenes): (1) the methyl group, (2) the phenyl group, and (3) the lone pair of electrons on the backbone nitrogen atom. Reactions at both the nitrogen atom<sup>39</sup> and the methyl group<sup>40</sup> in methyl and methyl/phenyl substituted cyclic phosphazenes {e.g.,  $[\text{Me}_2\text{PN}]_{3,4}$  and  $\text{Ph}_4\text{Me}_2\text{P}_3\text{N}_4$ } have been reported and serve as excellent models for reactions on the corresponding polymers. There is, however, very little work reported on the substitution reactions of the phenyl group in the cyclic phosphazenes.

#### A. Deprotonation/Substitution Reactions of P-Methyl Groups

The cyclic phosphazenes  $(\text{Me}_2\text{PN})_3$ ,  $(\text{Me}_2\text{PN})_4$ , and  $\text{Ph}_4\text{Me}_2\text{P}_3\text{N}_3$  have been deprotonated by butyllithium and the resulting anions quenched with electrophiles to yield phosphazenes with a variety of  $\text{PCH}_2\text{R}$  substituents (e.g., eq 24).<sup>41</sup> Surprisingly, the deprotonation reaction of the permethylated cyclics occurs completely, even if a deficiency of *n*-BuLi is used, so that 100% substitution (i.e., one R group per PN monomer unit) is easily achieved. Only with the tetraphenyl derivative  $\text{Ph}_4\text{Me}_2\text{P}_3\text{N}_3$  is it possible to obtain monosubstituted rings.



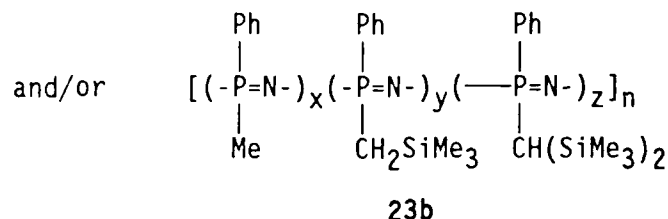
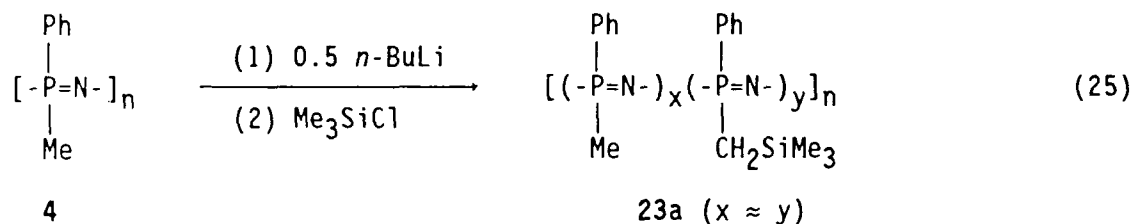
$\text{R} = \text{Me}, \text{Br}, \text{I}, \text{PhC(O)}, \text{CO}_2\text{H}, \text{AsMe}_2, \text{MMe}_3 \text{ (M = Si, Ge, Sn)}$

As discussed earlier, similar reactions can be carried out on the N-silylphosphoranimine precursors to the poly(alkyl/arylphosphazenes)<sup>23-26</sup> (see Section VB below) and, like the cyclic systems, can be used as models for the reactivity of poly(alkyl/arylphosphazenes). Related deprotonation/substitution reactions of the preformed polymers are under investigation in our labs and have resulted in the preparation of silylated polymers with reactive functional groups, polymers with alcohol side groups, carboxylated polymers and a water soluble derivative, and polystyrene grafted copolymers. In contrast to the chemistry of the permethylated cyclic phosphazenes, however, it has not yet been possible to achieve more than ca. 50% substitution (i.e., one functional group per two PN units). Several types of these reactions are discussed below.

1. *Reactions with Halides.* In 1986, we reported<sup>29</sup> the first derivatization reaction of a poly(alkyl/arylphosphazene). In this study, one-half of the methyl groups in  $[\text{Ph}(\text{Me})\text{PN}]_n$  (chosen for its solubility in THF as opposed to  $[\text{Me}_2\text{PN}]_n$  which is insoluble in THF and other ether solvents favorable for the deprotonation reaction) were deprotonated by treatment with 0.5 equivalents of *n*-BuLi at  $-78^\circ\text{C}$ . Subsequent addition of 0.5 equivalents of  $\text{Me}_3\text{SiCl}$  at  $-78^\circ\text{C}$  afforded the 50%-silylated derivative **23** (eq 25). While elemental analysis indicated complete incorporation of the  $\text{Me}_3\text{Si}$  group into the polymer, it is especially noteworthy that SEC (size exclusion chromatography) analysis showed that *no cleavage of the P-N backbone occurred*. In fact, the  $M_w$  of the  $\text{Me}_3\text{Si}$  derivative **23** was 26% higher than that of the parent polymer as expected for complete incorporation of the silyl groups. The molecular weight distributions as well as the intrinsic viscosities of the parent polymer **4** and the silylated product **23** were virtually identical. Presumably, it is the mild conditions of this reaction (i.e.,  $-78^\circ\text{C}$ ) that prevent chain degradation which occurs when poly(halophosphazenes) are treated with organolithium reagents<sup>6-9</sup>.

While the simplest representation of the silylated polymer is **23a**, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra suggested that deprotonation occurred more than once on some of the methyl groups producing polymer **23b** with  $\text{CH}(\text{SiMe}_3)_2$  groups as well as  $\text{CH}_2\text{SiMe}_3$  and unreacted methyl groups. The number of  $\text{CH}(\text{SiMe}_3)_2$  groups increases when the reaction is carried out under more dilute conditions (i.e., less than ca. 0.6 M) and

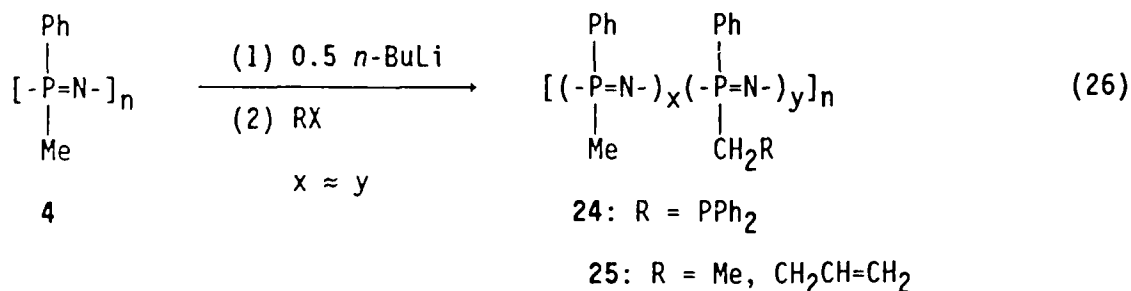
when  $[\text{Ph}(\text{Me})\text{PN}]_n$  is treated first with 0.5 equivalents of  $n\text{-BuLi}$  and then with two 0.25-equivalent portions of  $\text{Me}_3\text{SiCl}$  at one hour intervals. These conditions presumably favor the rearrangement (via  $\text{H}^+$  migration from a pendent  $\text{P-CH}_2\text{SiMe}_3$  to a  $\text{P-CH}_2^-$  center) of the polymeric anion to a more thermodynamically stable form containing a significant number of  $\text{P-C}(\text{SiMe}_3)\text{H}^-$  sites.



The thermal stability of the silyl substituted polymers **23** is very interesting since the onset of decomposition ( $391^\circ\text{C}$ ) is ca.  $30^\circ\text{C}$  higher than that of the parent polymer,  $[\text{Ph}(\text{Me})\text{PN}]_n$  (**4**). This is analogous to the higher thermal stability of the phosphoranimine  $\text{Me}_3\text{SiN}=\text{P}(\text{OCH}_2\text{CF}_3)(\text{CH}_2\text{SiMe}_3)\text{Me}$  relative to its non-silylated analogue **1**.<sup>23,24</sup>

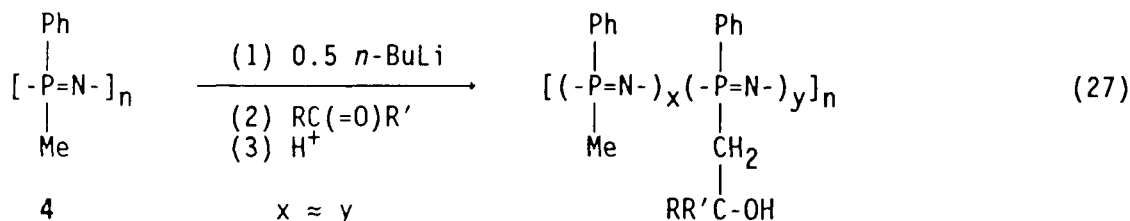
A series of related polymers  $\{[\text{Ph}(\text{Me})\text{PN}]_x[\text{Ph}(\text{RMe}_2\text{SiCH}_2)\text{PN}]_y\}_n$  [where  $\text{R} = \text{H}$ ,  $\text{CH}=\text{CH}_2$ , and  $\text{CH}_2(\text{CH}_2)_2\text{C}\equiv\text{N}$ ] have been prepared in the same fashion. These materials offer the possibility of further derivatization via the Si-H bond, the unsaturated vinyl moiety, or the cyano group and indicate that many other functional groups may be attached to the backbone through the  $\text{CH}_2\text{Si}$  spacer group. Several polymers with the same  $\text{RMe}_2\text{Si}$  substituents on 20% of the PN monomer units have also been prepared by treatment of **4** with 0.2 equivalents of  $n\text{-BuLi}/\text{RMe}_2\text{SiCl}$ .

These deprotonation/substitution reactions have also been carried out with other inorganic halides<sup>42</sup> (i.e.,  $\text{Ph}_2\text{PCl}$ ) and with several organic<sup>43</sup> halides (e.g.,  $\text{MeI}$ ,  $\text{CH}_2=\text{CHCH}_2\text{Br}$ ) (eq 26). The attachment of phosphine moieties (**24**) in this manner compliments that discussed before, in that it allows for the preparation of high molecular weight polymers with as many as one phosphine substituent per two PN repeat units. Similarly, use of allyl bromide permits attachment of the vinyl functional group (**25**;  $\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$ ) which can be used as a crosslinking site.



**2. Reactions with carbonyl containing electrophiles.** The reactivity of the polymeric anion toward electrophiles has been further demonstrated by its reactions with aldehydes and ketones (eq 27).<sup>44,45</sup> Treatment of the anion with these carbonyl compounds, containing both aliphatic and aromatic groups, and subsequent quenching of the alkoxy anion with a saturated aqueous solution of  $\text{NH}_4\text{Cl}$  resulted in a series of new polymers **26** in which 30 to 50% of the methyl groups were functionalized. In general, when the reactions were carried out by generation of the polymer anion at  $-78^\circ\text{C}$  with 0.5 equivalents of  $n\text{-BuLi}$ , stirring one hour, and adding the quench at  $-78^\circ\text{C}$ , the aldehydes reacted cleanly to give 45 to 50% substitution while the ketones typically produced polymers with only 20 to 30% of the methyl groups substituted. If, instead, the anion was allowed to warm to  $0^\circ\text{C}$  before addition of the ketone, higher degrees of substitution were obtained (30 to

40%). This implies that the polymer anion is more thermally stable than expected and that nucleophilic attack at the carbonyl carbon is favored over quenching of the anion by abstraction of a proton from the carbon  $\alpha$  to the carbonyl group, a problem which does not exist with the aldehydes. These polymers were fully characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  (including DEPT experiments which allowed for assignments of all chemical shift values), and  $^{31}\text{P}$  NMR spectroscopy, IR spectroscopy, elemental analysis, and SEC, with the latter again confirming that no chain degradation occurred as was shown with the silylation reactions.

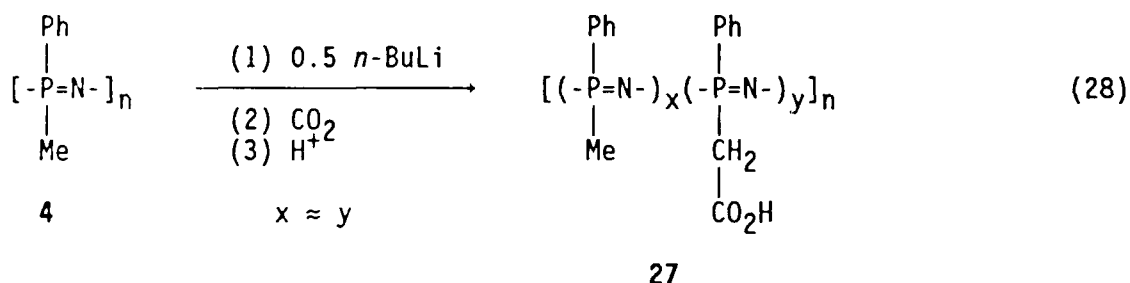


Fc = ferrocenyl

26	a	b	c	d	e	f
R	H	H	Me	Me	H	Me
R'	Ph	Me	Me	Ph	Fc	Fc

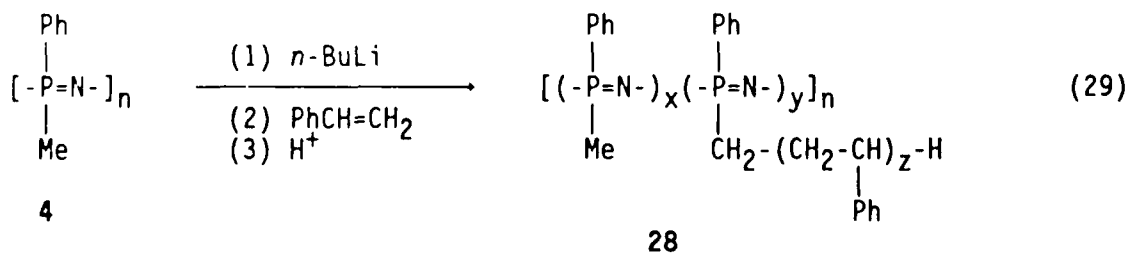
Perhaps the most interesting of these derivatives is **26e** which contains approximately one ferrocenyl moiety for every two PN repeat units<sup>44</sup>. By thermogravimetric analysis, the onset of decomposition of this compound was ca. 360°C, with a slight deflection at ca. 100°C. More importantly, the weight retained above 800°C (53%) is remarkably high for polyphosphazenes which generally tend to form cyclics that sublime leaving very little residue after thermolysis.

Poly(alkyl/arylphosphazenes) containing the carboxylate functional group (**27**) have also been prepared by a similar reaction sequence in which  $\text{CO}_2$  is used as the electrophile (eq 28). At the 50% substitution level, the polymer is insoluble in water, but readily becomes soluble on conversion to its sodium salt. Recent experiments suggest that even the carboxylic acid derivatives are somewhat water soluble if



the degree of substitution is increased (i.e., above 50%) by using one or more equivalents of  $n\text{-BuLi}$  and stirring at 0°C rather than at -78°C, conditions which favored higher degrees of substitution for the ketone reactions discussed above. The carboxylic acid derivatives **27** provide access to many other types of functionalization reactions, including crosslinking by typical organic condensation polymerization reactions.

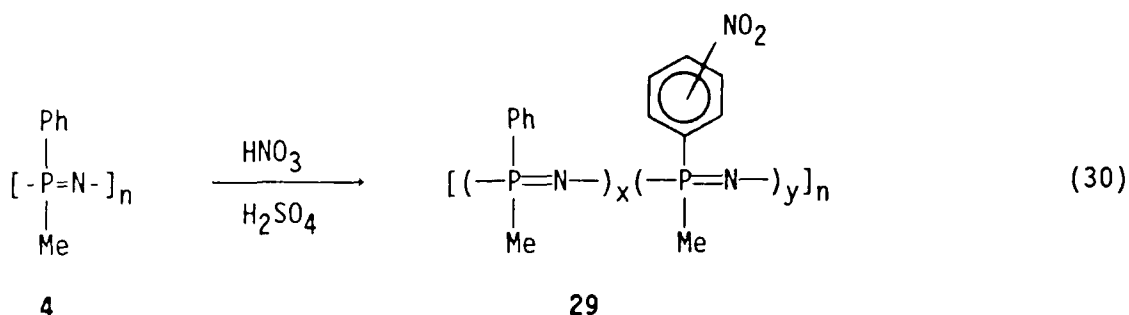
**3. Graft copolymers.** The anions generated on  $[\text{Ph}(\text{Me})\text{PN}]_n$  have also been used to initiate the anionic polymerization of styrene<sup>43,46</sup> resulting in graft copolymers **28** (eq 29) with both organic and inorganic components<sup>47</sup>. Based on control experiments which were carried out simultaneously with the



grafting reactions, copolymers with chain lengths of ca. 150, 50 and 20 styrene monomer units have been attached to 10-20% of the PN monomer units. Size exclusion chromatographic analysis and membrane osmometry indicated significant molecular weight increases as a result of grafting (ca. 300,000 to 650,000), whereas physical blends of polystyrene and **4** had SEC traces clearly representative of mixtures of the two components. Moreover, the viscosities of the grafts (ca. 1.4 to 3.3 dL/g) were markedly higher than that of similar blends (ca. 0.2 dL/g). **These reactions clearly demonstrate the feasibility of using poly(alkyl/arylphosphazenes) as backbones in other inorganic/organic and inorganic/inorganic graft copolymers.**

### B. Substitution Reactions of P-Phenyl Rings

The attachment of the substituents in poly(alkyl/arylphosphazenes) by direct P-C bonds should enhance the chemical stability of the P-N backbone, thus making possible the use of a greater variety of reagents and rather severe reaction conditions in derivatization reactions. An example of this is the nitration of the phenyl substituent in  $[\text{Ph}(\text{Me})\text{PN}]_n$  (**4**) with nitric and sulfuric acids at 50°C (eq 30).<sup>48</sup> Reaction

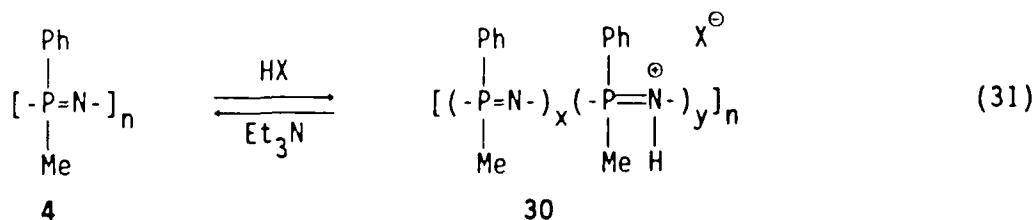


times of 15, 30, 60, 90, and 170 minutes produced the nitrated derivatives **29** as light yellow, film-forming materials. Both <sup>31</sup>P NMR spectroscopy and SEC analysis indicated that these products were still polymeric. The SEC molecular weights were, however, lower and the molecular weight distributions were narrower than that of the parent polymer. Interestingly, the *apparent* molecular weight showed a very small, but steady, decrease (from ca. 60,000 to 50,000 over the entire range of times) with the reaction time. These results suggest that the solution properties of the derivatized polymers have been altered by the polar NO<sub>2</sub> groups, while the actual polymer chain length is probably unchanged.

### C. Reactions of the Backbone Nitrogen

The third potentially reactive site in polyphosphazenes is the backbone nitrogen. In fact, the backbone nitrogens in poly(alkyl/arylphosphazenes) should be particularly good donors because of the electron releasing nature of the organic substituents attached directly to phosphorus. This is indeed the case for the cyclic methyl phosphazenes,  $[\text{Me}_2\text{PN}]_n$  ( $n = 3, 4, 5$ ), which form stable salts with HCl, HClO<sub>4</sub>, and alkyl iodides.<sup>49</sup> Interestingly, the cyclic trimer undergoes protonation or methylation at only one of the nitrogen atoms per ring, whereas, the tetramer and pentamer can readily take on either one or two substituents per ring at the nitrogen centers.

The analogous chemistry of the *polymeric* alkyl/arylphosphazenes has not yet been extensively studied. Preliminary work in our laboratories, however, strongly suggests that the same types of reactions are possible. For example, treatment of CH<sub>2</sub>Cl<sub>2</sub> or THF solutions of poly(methylphenylphosphazene) (**4**) with several acids (either anhydrous or aqueous) leads to precipitation of protonated polymers **30** (eq 31). Addition of excess Et<sub>3</sub>N results in regeneration of the parent polymer as confirmed by NMR spectroscopic and SEC analysis. In the case of the HI salt, the degree of protonation was found to be ca. 68% both by the mass balance of the reaction and by the elemental analysis of the protonated polymer.



Such reactions do not always occur without damage to the polymer chain. For example, the high temperature interaction of preformed poly(alkyl/arylphosphazene) with  $\text{Me}_3\text{SiBr}$  results in complete cleavage of the polymer chains to give cyclic phosphazenes. In fact, this reaction occurs even under milder conditions (refluxing benzene solution). It seems likely that P-N bond cleavage could result from nucleophilic attack of the counter ion (e.g.,  $\text{Br}^-$ ) on a phosphorus center that is adjacent to a silylated nitrogen, although this hypothesis has not been verified experimentally.

## Summary

This report has focused on the synthesis and characterization of polyphosphazenes with only P-C bonded substituents at phosphorus and on relevant chemistry of the Si-N-P precursors to these polymers. Polyphosphazenes with simple alkyl and aryl groups attached to the backbone are readily prepared in essentially quantitative yields by the condensation polymerization of N-silylphosphoranimines,  $\text{Me}_3\text{SiN}=\text{P}(\text{X})\text{RR}'$ . This approach allows for the incorporation of the substituents at the small molecule stage, is facilitated by the ease of separation of the volatile silane byproducts from the polymers, and may potentially offer control of molecular weights through variation of leaving groups (X and  $\text{R}_3\text{Si}$ ) and thermolysis conditions. The condensation method can also be used for the preparation of a variety of copolymers with certain functional groups that are unreactive at the polymerization temperature. In addition to its importance in the synthesis of poly(alkyl/arylphosphazenes), the condensation polymerization process may serve as a model for the preparation of other polymers with main group element backbones.

While the mechanism of this condensation polymerization is not fully understood, it appears to be a chain growth process, probably initiated by heterolytic cleavage of the polar  $\text{P}^{\delta+}-\text{X}^{\delta-}$  bond. Nonetheless, the poly(alkyl/arylphosphazenes) which result have been well characterized and exist as extended, flexible chains in solvents such as THF or  $\text{CHCl}_3$  with average chain lengths of several hundred to a thousand repeat units and relatively narrow molecular weight distributions (i.e.,  $M_w/M_n \approx 2$ ).

Derivatization reactions of the simple poly(alkyl/arylphosphazenes), obtained from the condensation process, are also the source of new polymers with functionalized side groups. Through deprotonation/substitution reactions at the pendent methyl groups or electrophilic aromatic substitutions on the phenyl groups, ferrocenyl, alcohol, silyl and functionalized silyl, carboxylate, amino, nitro, and polystyrene groups have been attached to the polymers. The backbone nitrogen atoms are easily protonated, suggesting that Lewis acid coordination reactions may also be general processes for these systems. These straightforward reactions on the preformed polymers indicate that it should be possible to widely vary the chemical and physical properties of the P-C substituted phosphazenes by the attachment of many other functional groups, particularly those which cannot be attached to the phosphoranimine precursors, which do withstand the polymerization conditions, or which inhibit thermal polymerization.

The chemistry of the condensation polymer precursors has also been investigated. This has involved the synthesis of (silylamino)phosphines,  $(\text{Me}_3\text{Si})_2\text{NPRR}'$ , with a variety of substituents (R and  $\text{R}'$ ); studies of the most feasible methods of oxidizing these to the immediate polymer precursors, the N-silylphosphoranimines,  $\text{Me}_3\text{SiN}=\text{P}(\text{X})\text{RR}'$ ; and studies of the reactivity of the phosphoranimines, including transsilylation reactions, variation of the leaving group (X), and modification of the R and  $\text{R}'$  side groups. This work has resulted in a less costly route to the polymers via the use of phenoxy rather than trifluoroethoxy leaving groups and in the preparation of functionalized phosphoranimines which can be easily converted to some new polymers. The side-group derivatization reactions also serve as models for reactions that can be carried out on the preformed polymers.

The P-C substituted polyphosphazenes offer another dimension to the already broad field of phosphazene polymers. The condensation polymerization and derivatization reactions of its products fully complement the ring-opening/substitution methods which have produced a large number of P-O and P-N substituted and several P-O/P-C substituted polyphosphazenes. It is clear, therefore, that phosphazenes are the most diverse class of inorganic polymers and that they will have a significant impact in the wide spread search for new materials. This relatively young class of polymers has already produced materials which can be used as electrical conductors, flame retardants, biomedical materials, and low temperature elastomers. It is the very ease of attachment of such a large array of side groups by a variety of methods that allows for such diverse applications of polyphosphazenes and for the custom design of properties suitable for specific applications.

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## List of Publications

- Wisian-Neilson, P.; Ford, R. R.; Goodman, M. A.; Li, B.-L.; Roy, A. K.; Wettermark, U. G.; Neilson, R. H. "Reactions of (Silylamino)phosphines with Carbon Tetrachloride" *Inorg. Chem.* **1984**, 23, 2063.
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